

Appendix 3.1 Composition Models

A.3.1.1 Geophysical Fluid Dynamics Laboratory

Composition changes for the short-lived species from 2000 to 2100 in the GFDL experiments were calculated using the global chemical transport model MOZART-2 (Model for Ozone And Related chemical Tracers, version 2.4), which has been described in detail previously (Horowitz *et al.*, 2003; Horowitz, 2006; and references therein. This model was used to generate distributions of ozone, sulfate, black and organic carbon, and dust for the emission scenarios discussed in Section 3.2.1. Emissions and initial conditions for methane were scaled each decade to match the global average methane abundances specified in the A1B “marker” scenario. The model includes 63 gas-phase species, 11 aerosol and precursor species to simulate sulfate, nitrate, ammonium, and black and organic carbon and five size bins for mineral dust (diameter size bins of 0.2-2.0 μm , 2.0-3.6 μm , 3.6-6.0 μm , 6.0-12.0 μm , and 12.0-20.0 μm). Hydrophobic black and organic carbon are chemically transformed into hydrophilic forms with a lifetime of 1.63 days (Tie *et al.*, 2005). Different aerosol types are assumed to be externally mixed and do not interact with one another. Sulfur oxidation in the gas phase and within clouds is fully interactive with the gas-phase oxidant chemistry.

The transport in MOZART-2 is driven with meteorological inputs provided every three hours by the middle-atmosphere version of the NCAR Community Climate Model (Kiehl *et al.*, 1998). The meteorology was the same for each decade, thus excluding any feedbacks from climate change on natural emissions and rates of chemical reactions and removal. Thus, natural emissions, such as those of isoprene, dust, and NO_x from

lightning, are held constant at present-day levels. Convective mass fluxes are re-diagnosed from the large-scale meteorology using the Hack (1994) and Zhang and McFarlane (1995) schemes. Vertical diffusion within the boundary layer is diagnosed using the scheme of Holtslag and Boville (1993). Tracer advection is performed using a flux-form semi-Lagrangian scheme (Lin and Rood, 1996).

The horizontal resolution is 2.8° latitude x 2.8° longitude, with 34 hybrid sigma-pressure levels extending up to 4 hPa. Photolysis frequencies for clear-sky are interpolated from a pre-calculated lookup table, based on a standard radiative transfer calculation (TUV version 3.0; (Madronich and Flocke, 1998). The values are modified to account for cloudiness (Brasseur *et al.*, 1998), but do not account for effects of the simulated aerosols. Heterogeneous hydrolysis of N_2O_5 and NO_3 on aerosol surfaces occurs at a rate based on the simulated sulfate surface area, with a reaction probability = 0.04 (Tie *et al.*, 2005). Stratospheric concentrations of ozone and several other long-lived gases are relaxed to present-day climatological values.

Dry deposition velocities for gas-phase species are calculated off-line using a resistance-in-series scheme (Wesely, 1989). Deposition velocities for aerosol species are prescribed as by Tie *et al.* (2005). Wet removal of soluble species in and below clouds is included as a first-order loss process, based on the large-scale and convective precipitation rates, as described by Horowitz *et al.* (2003). In-cloud scavenging is based on the parameterization of Giorgi and Chameides (1985), while below-cloud washout of highly soluble species follows Brasseur *et al.* (1998). For gas-phase species, the removal rate

depends strongly on the temperature-dependent effective Henry's law constant. Wet deposition of soluble aerosols (sulfate, hydrophilic BC, hydrophilic OC, ammonium, and nitrate) is calculated by scaling the removal rate to that of highly-soluble HNO_3 , assuming the aerosols have a first-order loss rate constant equal to 20% of that of HNO_3 (Tie *et al.*, 2005). This scaling introduces a large uncertainty into the calculation of aerosol burdens. The sensitivity of model results to this scale factor is discussed below (Section 5). Wet removal of dust is calculated using the formulation of Zender *et al.* (2003), with below-cloud scavenging efficiencies of $0.02 \text{ m}^2 \text{ kg}^{-1}$ for convective and $0.04 \text{ m}^2 \text{ kg}^{-1}$ for stratiform precipitation.

The ozone and aerosol distributions from these simulations have been evaluated by Horowitz (2006) and Ginoux *et al.* (2006), respectively. Simulated ozone concentrations agree well with present-day observations and recent trends (Horowitz, 2006). Overall, the predicted concentrations of aerosol are within a factor 2 of the observed values and have a tendency to be overestimated (Ginoux *et al.*, 2006). The annual mean surface sulfate concentrations match observed values within a factor 2 with values ranging from $0.05 \mu\text{g m}^{-3}$ in the remote marine atmosphere to $13 \mu\text{g m}^{-3}$ in polluted regions. In general, the simulated concentrations are over-predicted in summer and under-predicted in winter. Sulfate mass column and zonal mean profiles are comparable to previous studies, although the global mean burden is about 15% higher. The annual mean concentration of carbonaceous aerosols is generally overestimated in polluted regions by up to a factor of 2. An exception is West Africa where other models show significant loadings of carbonaceous aerosols associated with biomass burning activities during the dry season

while our results do not show any perturbation arising from such activities. The source of this discrepancy seems to be caused in part by the emission inventory in West Africa. The annual mean dust concentration at the surface agrees with the observations to within a factor 2, except over Antarctica where it is underestimated by a factor of 5.

The three-dimensional monthly mean distributions of ozone, black and organic carbon aerosol, and sulfate aerosol from MOZART-2 were archived from simulations for each decade from 2000 to 2100. The results from these simulations were then interpolated to intermediate years and used in the transient climate simulations. The distribution of dust from a present-day simulation in MOZART-2 was used in all years of the climate simulations.

A.3.1.2 Goddard Institute for Space Studies

The configuration of the GISS composition model used here has been described in detail in (Shindell *et al.*, 2007). The composition model PUCCINI (Physical Understanding of Composition-Climate INteractions and Impacts) includes ozone and oxidant photochemistry in both the troposphere and stratosphere (Shindell *et al.*, 2006). Photochemistry includes 155 reactions. The model calculates the abundances of 51 chemical species, 26 of which are transported by the model's advection scheme. It uses 'lumped families' for hydrocarbons and PANs. Chemical reactions involving these surrogates are based on the similarity between the molecular bond structures within each family using the reduced chemical mechanism of (Houweling *et al.*, 1998). This mechanism is based on the Carbon Bond Mechanism-4 (CBM-4) (Gery *et al.*, 1989),

modified to better represent the globally important range of conditions. The CBM-4 scheme has been validated extensively against smog chamber experiments and more detailed chemical schemes. This scheme was modified for use in global models by removing aromatic compounds and adding in reactions important in background conditions, including organic nitrate and organic peroxide reactions, and extending the methane oxidation chemistry. The revised scheme was then readjusted based on the more extensive Regional Atmospheric Chemistry Model (RACM) (Stockwell *et al.*, 1997), and the modified scheme includes several surrogate species designed to compensate for biases relative to the RACM mechanism. The modified scheme was shown to agree well with the detailed RACM reference mechanism over a wide range of chemical conditions including relatively pristine environments (Houweling *et al.*, 1998).

Rate coefficients are taken from the NASA JPL 2000 handbook (Sander *et al.*, 2000). Photolysis rates are calculated using the Fast-J2 scheme (Bian and Prather, 2002), except for the photolysis of water and nitric oxide (NO) in the Schumann-Runge bands, which are parameterized according to (Nicolet, 1984; Nicolet and Cieslik, 1980). The aerosols component simulates sulfate, carbonaceous and sea-salt aerosols (Koch *et al.*, 2007; Koch *et al.*, 2006) and nitrate aerosols (Bauer *et al.*, 2006). It includes prognostic simulations of DMS, MSA, SO₂ and sulfate mass distributions. The mineral dust aerosol model transports four different sizes classes of dust particles with radii between 0.1-1, 1-2, 2-4, and 4-8 microns (Miller *et al.*, 2006). Most importantly, these components interact with

one another, with linkages including oxidants affecting sulfate, gas-phase nitrogen species affecting nitrate, sulfate affecting nitrogen heterogeneous chemistry via reaction of N_2O_5 to HNO_3 , and sulfate and nitrate being absorbed onto mineral dust surfaces (*i.e.*, the aerosols are internally mixed as coatings form on dust surfaces (Bauer *et al.*, 2006). The latter is described by a pseudo first-order rate coefficient which gives the net irreversible removal rate of gas-phase species to an aerosol surface. We use the uptake coefficient of 0.1 recommended from laboratory measurements (Hanisch and Crowley, 2001), though this value is fairly uncertain.

Phase transformation and removal of soluble species is calculated using a wet deposition scheme in which soluble gases can be removed into either moist convective plumes or large-scale clouds as derived from the GCM's internal cloud scheme (Del Genio and Yao, 1993). During convection, all chemical species are transported along with the convective plumes, with scavenging of soluble species within and below cloud updrafts. In large-scale stratiform clouds, soluble gases are removed based on the fraction of the grid box over which precipitation is taking place. Washout of soluble species is calculated below precipitating clouds. In the case of either evaporation of precipitation before reaching the ground, or detrainment or evaporation from a convective updraft, the dissolved species are returned to the air. Wet chemistry calculations take place in each grid box at each time step, including the coupling with the convection scheme's entraining and nonentraining plumes (which are based on the convective instability in the particular grid box at that time), so are entirely consistent with the contemporaneous model physics. The solubility of each gas is determined by an effective Henry's Law

coefficient, assuming a pH of 4.5. Surface dry deposition is calculated using a resistance-in-series model (Wesely and Hicks, 1977) coupled to a global, seasonally varying vegetation data set as given by (Chin *et al.*, 1996).

The 2000 simulation uses the 2000 emission inventory of the International Institute for Applied Systems Analysis (IIASA), except for biomass burning which is taken from the Global Fire Emission Database (GFED) averaged over 1997-2002 (Van der Werf *et al.*, 2003) with emission factors from (Andrae and Merlet, 2001) for aerosols. The IIASA inventory is based on the 1995 EDGAR3.2 inventory (Olivier and Berdowski, 2001), extrapolated to 2000 using national and sector economic development data (Dentener *et al.*, 2005). Lightning NO_x emissions are calculated internally in the GCM (5.6 Tg/yr for present-day), and other natural sources are prescribed according to conventional estimates. Dust emissions are constant at 1580 Tg/yr, while isoprene emissions are 356 Tg/yr. Emissions of DMS are 41 Tg/yr.

The simulations described here were run with this composition model included within a 23-layer (up to 0.01 hPa), 4° x 5° horizontal resolution version of the ModelE climate model (Schmidt *et al.*, 2006). This composition model was used for both the transient climate and regional/sector emissions perturbation simulations.

Present-day composition results in the model are generally similar to those in the underlying chemistry and aerosol models documented previously. The model used here does not include the enhanced convective scavenging of insoluble species prescribed in

(Koch *et al.*, 2007). Therefore our carbonaceous aerosol burden, especially in the free troposphere, is nearly double that of (Koch *et al.*, 2007). Comparison with the limited available observations is comparable between the two simulations (a positive bias replaces a negative bias).

A.3.1.3 National Center for Atmospheric Research

Various methods were used at NCAR to estimate future composition. Present-day tropospheric ozone was taken from calculations performed by Lamarque *et al.* (2005) using the MOZART-2 model; beyond 2000, tropospheric ozone was calculated by T. Wigley using the MAGICC model (<http://www.cru.uea.ac.uk/~mikeh/software/magicc.htm>) forced by the time-varying emissions of NO_x, methane and VOCs and these average global values were used to scale the present-day distribution. Future carbonaceous aerosols were scaled from their present-day distribution (Collins *et al.*, 2001) by a globally uniform factor whose time evolution follows the global evolution of SO₂ emissions. Future levels of sulfate aerosols were calculated using the MOZART model. Stratospheric ozone changes are prescribed following the study by (Kiehl *et al.*, 1999).

The Model for Ozone and Related chemical Tracers version 2 (MOZART-2) is described by Horowitz *et al.* (2003) and references therein. The model provides the distribution of 80 chemical constituents (including nonmethane hydrocarbons) between the surface and the stratosphere. The model was run at a uniform horizontal resolution of ~2.8° in both latitude and longitude. The vertical discretization of the

3448 meteorological data (described below) and hence of the model consists of 18 hybrid
3449 levels from the ground to ~4 hPa. The evolution of species is calculated with a time
3450 step of 20 min.

3451 The tropospheric photolysis rates use a vertical distribution of ozone based on the
3452 simulated ozone in the troposphere and on the climatology from Kiehl *et al.* (1999)
3453 above. For each simulation, this latter distribution is updated to reflect the changes in the
3454 lower stratosphere during the 20th century, affecting only the photolysis rates and not the
3455 amount of ozone transported from the stratosphere.

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3457 The NCAR regional/sector perturbation simulations (Section 3.4) used a version of
3458 MOZART chemical transport model (Horowitz *et al.*, 2003) embedded within the
3459 Community Atmosphere Model (CAM3, Collins *et al.*, 2006). This model, known as
3460 CAM-chem, includes an extension of the chemical mechanism presented by Horowitz *et*
3461 *al.* (2003) to include an updated terpene oxidation scheme and a better treatment of
3462 anthropogenic non-methane hydrocarbons (NMHCs). The MOZART aerosols have been
3463 extended by Tie *et al.* (2001, 2005) to include a representation of ammonium nitrate that
3464 is dependent on the amount of sulfate and ammonia present in the air mass following the
3465 parameterization of gas/aerosol partitioning by Metzger *et al.* (2002). In brief, CAM-
3466 chem simulates the evolution of the bulk aerosol mass of black carbon (BC, hydrophobic
3467 and hydrophilic), primary organic (POA, hydrophobic and hydrophilic), second organic
3468 (SOA, linked to the gas-phase chemistry through the oxidation of atmospheric NMHCs
3469 as in (Chung and Seinfeld, 2002), ammonium and ammonium nitrate (from NH₃
3470 emissions), and sulfate aerosols (from SO₂ and DMS emissions). It also considers the

uptake of N_2O_5 , HO_2 , NO_2 , and NO_3 on aerosols. Results from the CAM-chem model are discussed by Lamarque *et al.* (2005b). A description of sea-salt, updated from Tie *et al.* (2005), is also included. Finally, a monthly-varying climatology of dust is used only for radiative calculations. The CAM-chem model considers only the direct effect of aerosols and the atmospheric model is coupled with the chemistry solely through the radiative fluxes, taking into account all radiatively active gases and aerosols. The horizontal resolution is 2° latitude x 2.5° longitude, with 26 levels ranging from the surface to ~ 4 hPa.